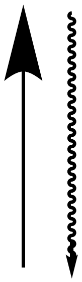
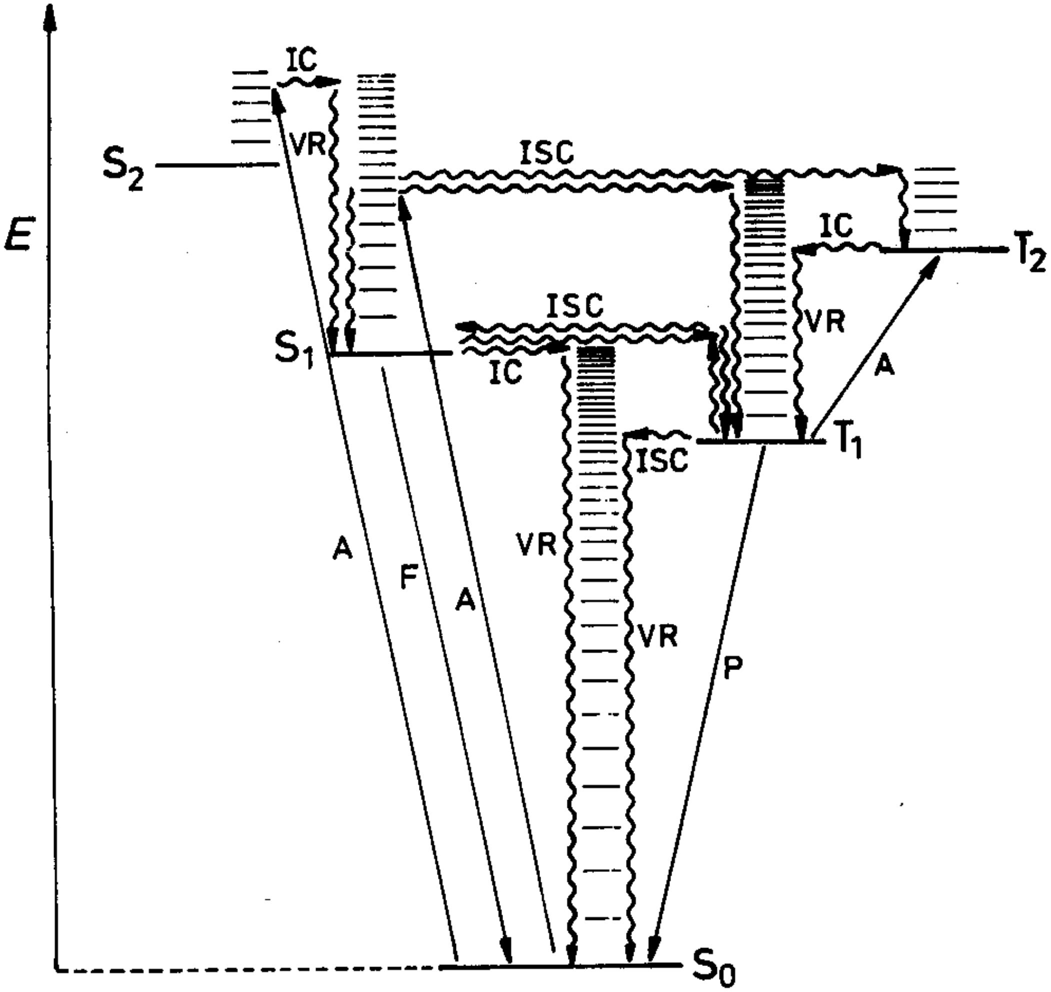
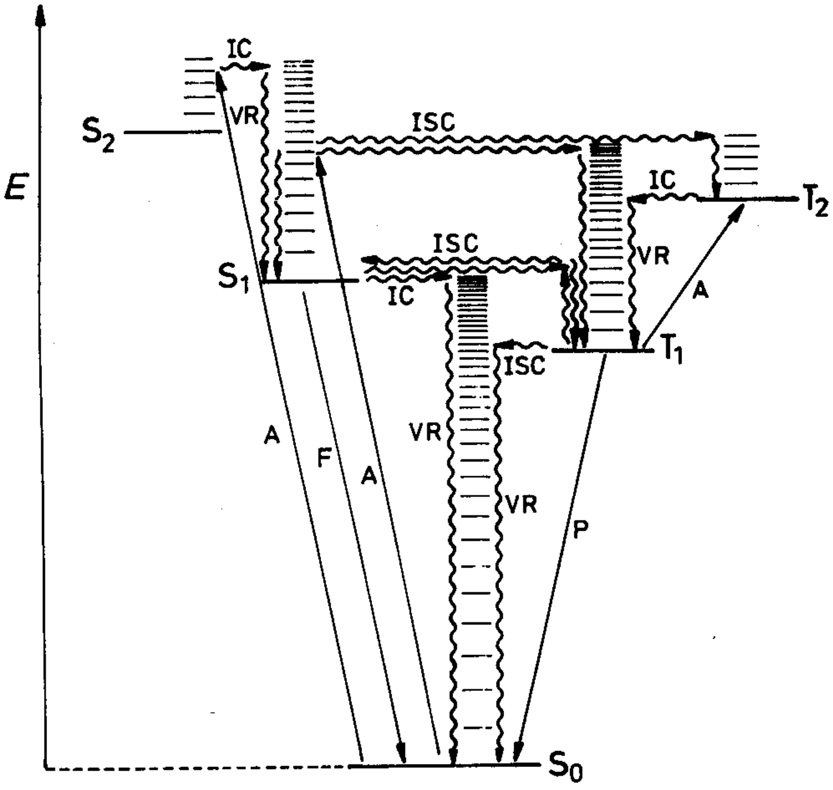
Radiationless Transition



Radiative and Radiationless Transitions



Radiationless Transitions Between States



$S_0 + h\nu \longrightarrow S_1$ spin allowed absorption

$S_1 \longrightarrow S_0 + h\nu$ spin allowed emission (fluorescence)

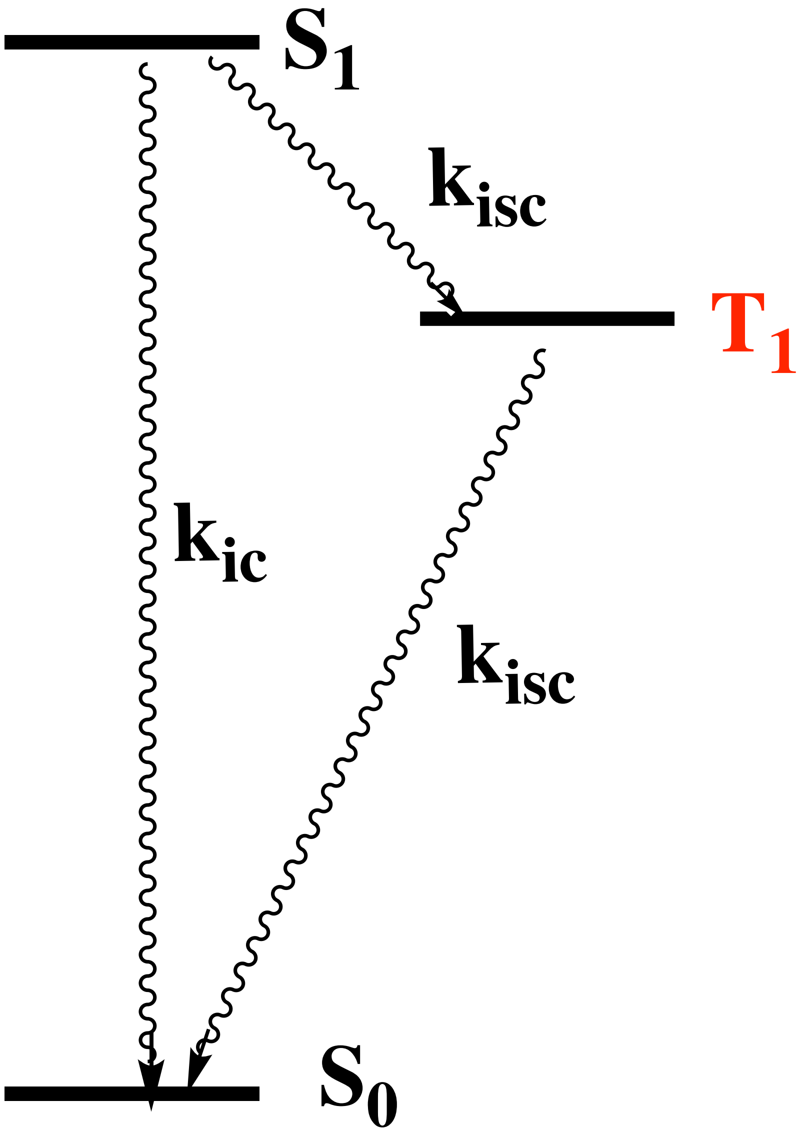
$\mathbf{S_1 \longrightarrow S_0 + \Delta}$ **spin allowed radiationless transition (internal conversation)**

$\mathbf{S_1 \longrightarrow T_1 + \Delta}$ **spin forbidden radiationless transition (intersystem crossing)**

$S_0 + h\nu \longrightarrow T_1$ spin forbidden absorption

$T_1 \longrightarrow S_0 + h\nu$ spin forbidden emission(phosphorescence)

$T_1 \longrightarrow S_0 + \Delta$ spin forbidden radiationless conversion (intersystem crossing)


S$_1$
k$_{isc}$
T$_1$
k$_{ic}$
k$_{isc}$
S$_0$

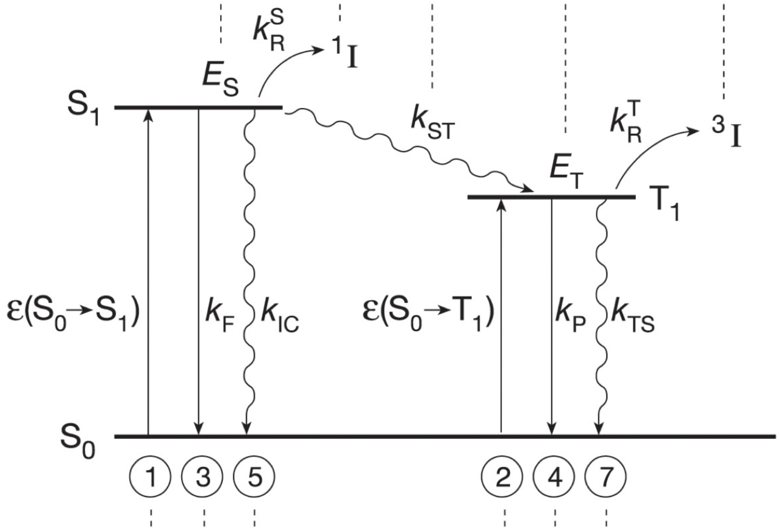
Why radiationless transitions matter?
Competition with fluorescence and phosphorescence

$$S_0 + h\nu \xrightarrow{I_{abs}} S_1$$

$$S_1 \xrightarrow{k_f} S_0 + h\nu$$

$$S_1 \xrightarrow{k_{isc}} T_1$$

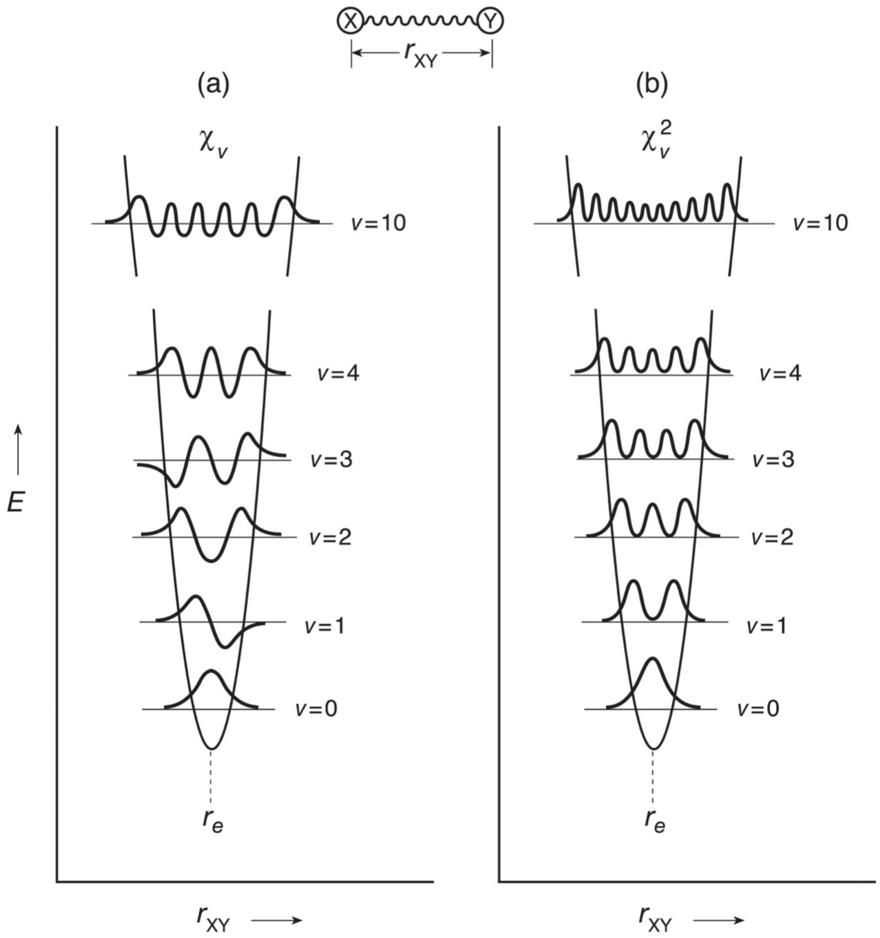
$$S_1 \xrightarrow{k_{ic}} S_0$$



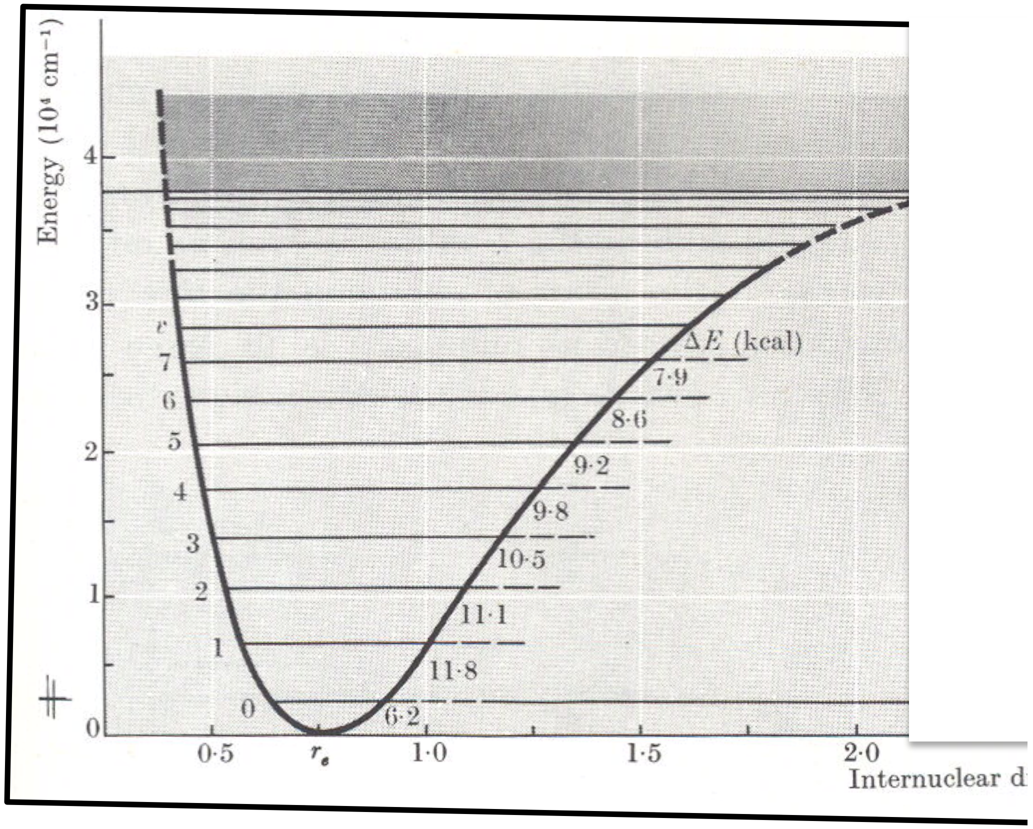
$$\phi_f = \frac{k_f[S_1]}{(k_f + k_{isc} + k_{ic} + \ldots)[S_1]}$$

$$\tau_f = \frac{1}{k_f + k_{isc} + k_{ic} + \ldots.}$$

Visualization of vibrational levels within an electronic energy surface

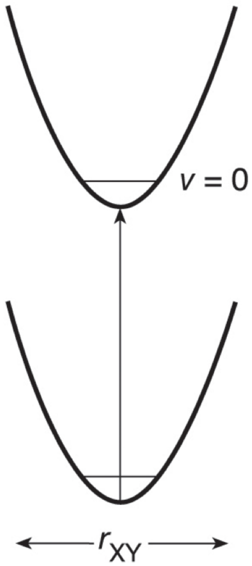


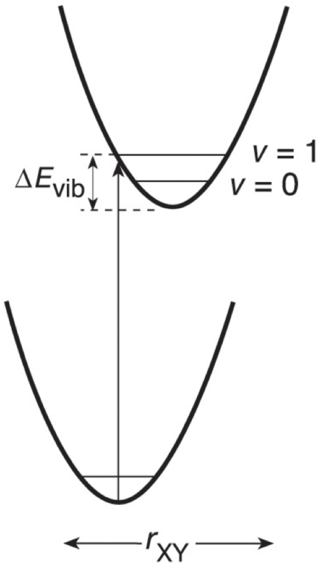
Harmonic

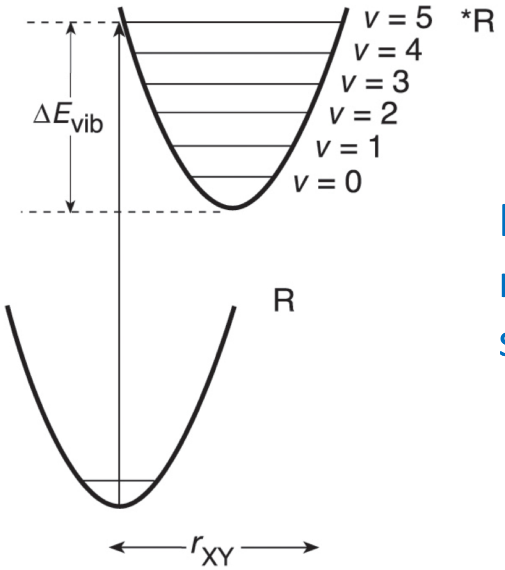


Anharmonic

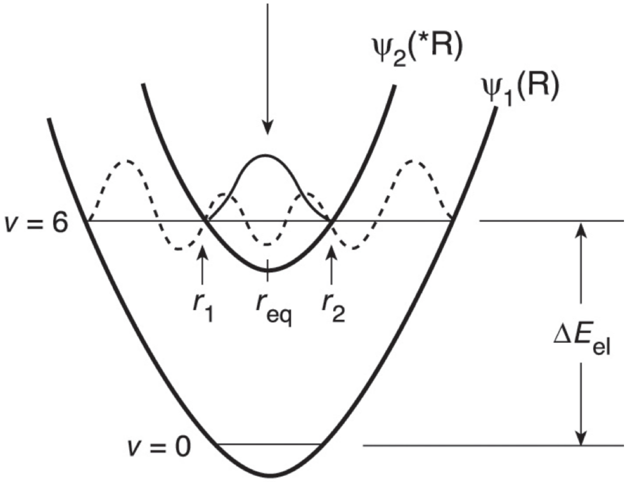
Visualization of vibrational levels within a ground state and excited state electronic energy surfaces



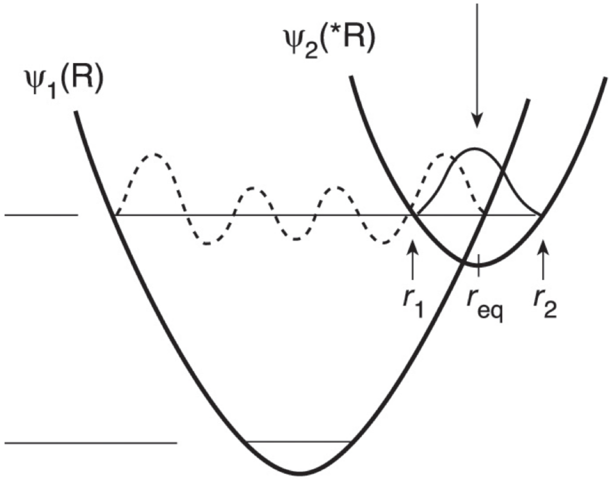




Note: the location of minimum on the upper surface



Matching surfaces



Crossing surfaces

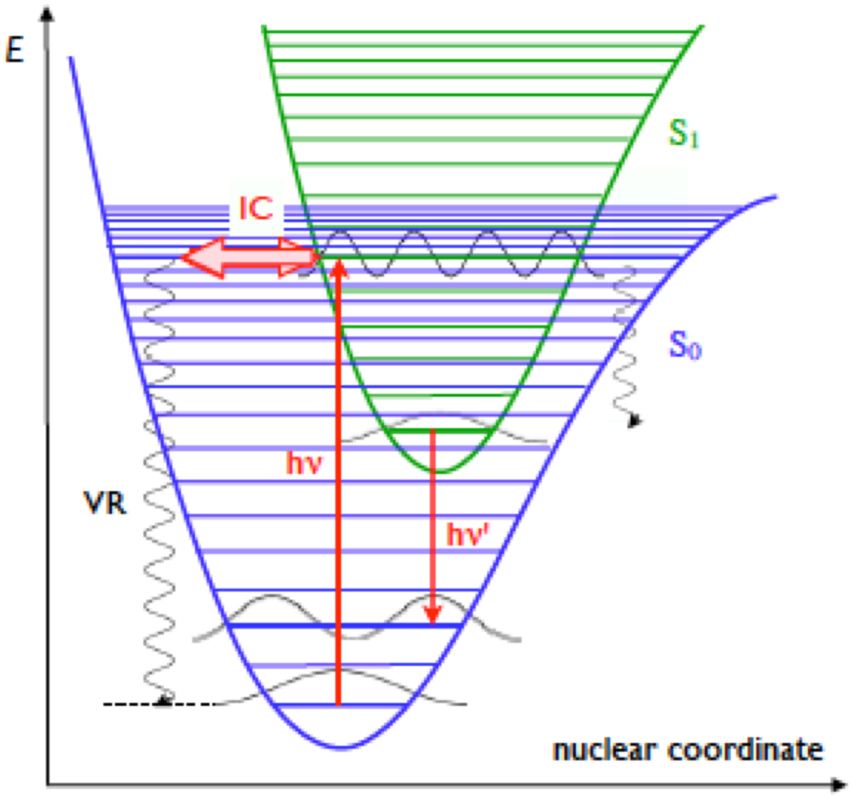
Conversion of electronic to vibrational energy

Three step process: (a) upper vibrational to lower vibrational level in excited state

(b) lower vibrational level to upper vibrational of the lower state

(c) upper vibrational of the lower state to lowest vibrational level

Non-radiative deactivation processes

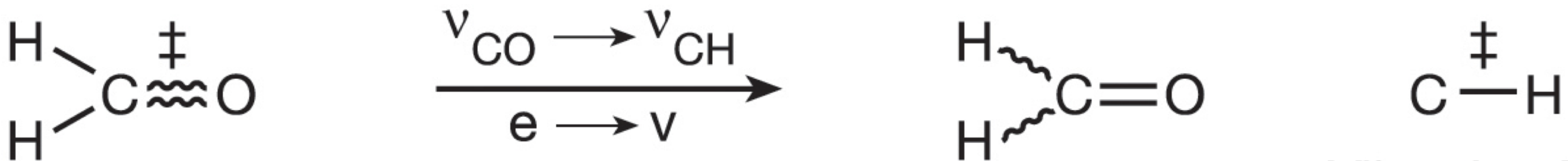


Internal conversion (IC) implies the transformation of electronic excitation into vibrational energy. This process takes place through *nuclear tunneling* from the excited state potential surface to that of the ground state. Strong overlap of vibrational wave functions is necessary.

Since back-tunneling can also readily occur, fast vibrational relaxation (VR) is an important condition for this deactivation pathway.

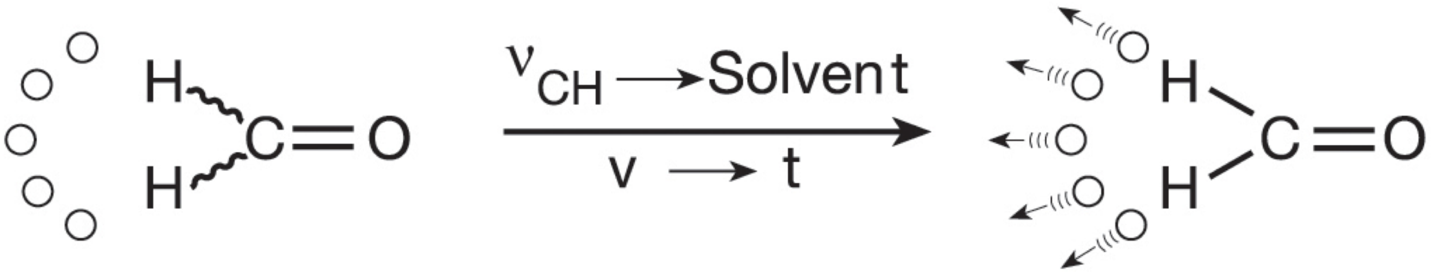
Electronic to Vibrational Energy Transfer

Intramolecular vibrational relaxation (**IVR**) occurs within 10 to 0.1 ps



Vibration **hot**

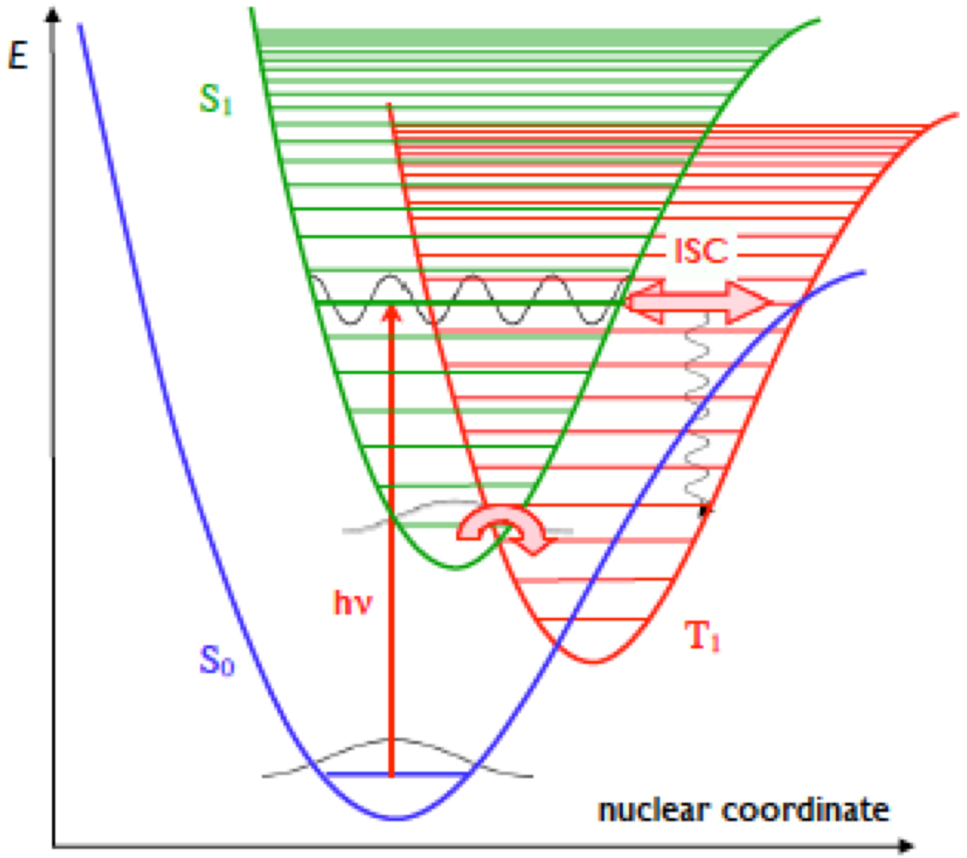
Intermolecular vibrational energy transfer (**VET**) from the molecule to the solvent occurs in the time range 100 to 10 ps



Solvent is **hot** (translations and vibrations)

Radiationless processes include (a) orbital symmetry and (b) spin selection rules

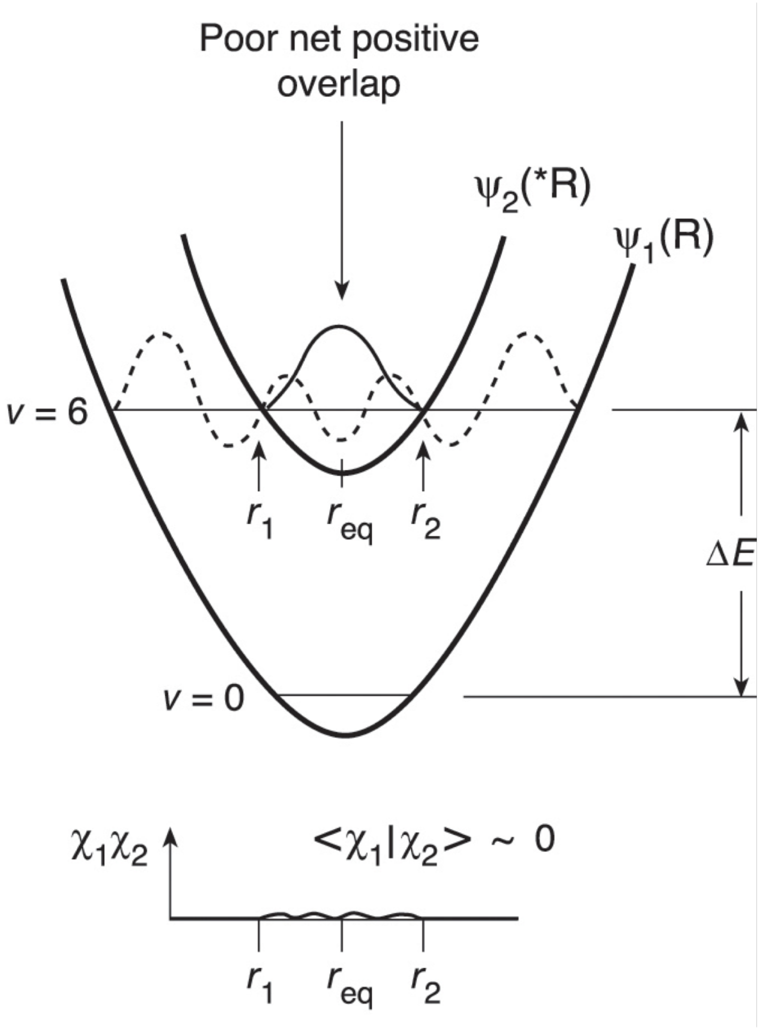
Non-radiative deactivation processes

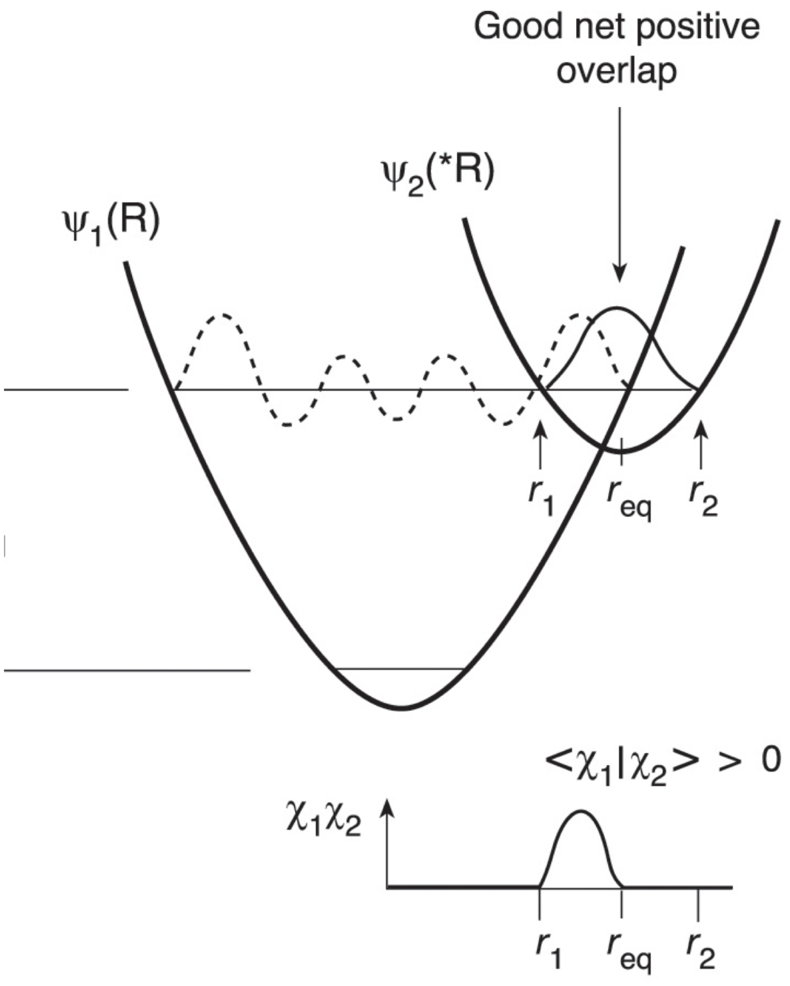


Intersystem crossing (ISC) is a special case of internal conversion, which takes place between an electronic excited state and another excited state characterized by a different spin multiplicity ($S_1 \rightarrow T_1$, for instance). This process involves a simultaneous spin flip.

Vibrational relaxation is also necessary to avoid crossing back to the initial system.

Radiationless Process and Surface Crossing and Matching





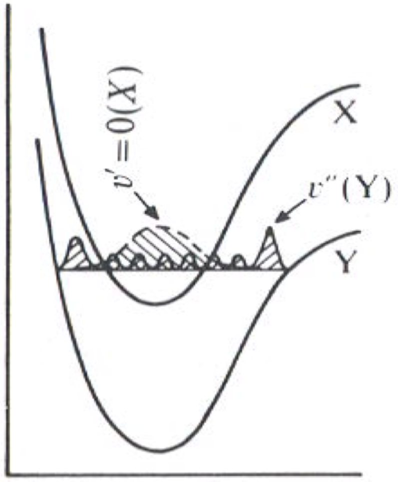
The Energy Gap Law for Internal Conversion

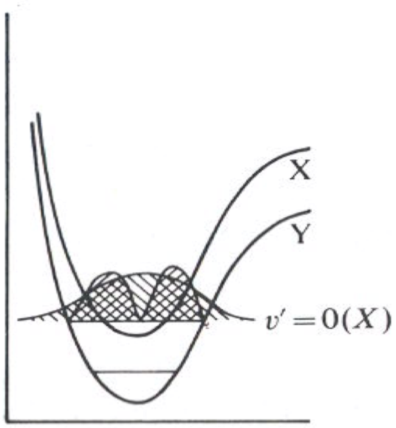
$$\boldsymbol{f \sim \exp\text{-}\Delta E}$$

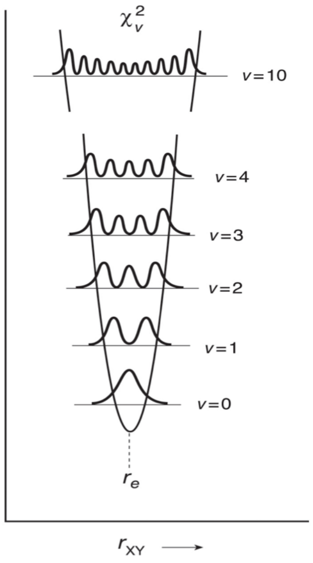
$$k_{IC} \sim 10^{13} f_{\nu}$$

$$k_{IC} \sim 10^{13}\exp\text{-}\alpha\Delta E$$

ΔE is the energy separation between the surfaces involved in the transition at the nuclear geometry r_c.







Dependence of rate of k_{IC} S_1 to S_0 on energy gap

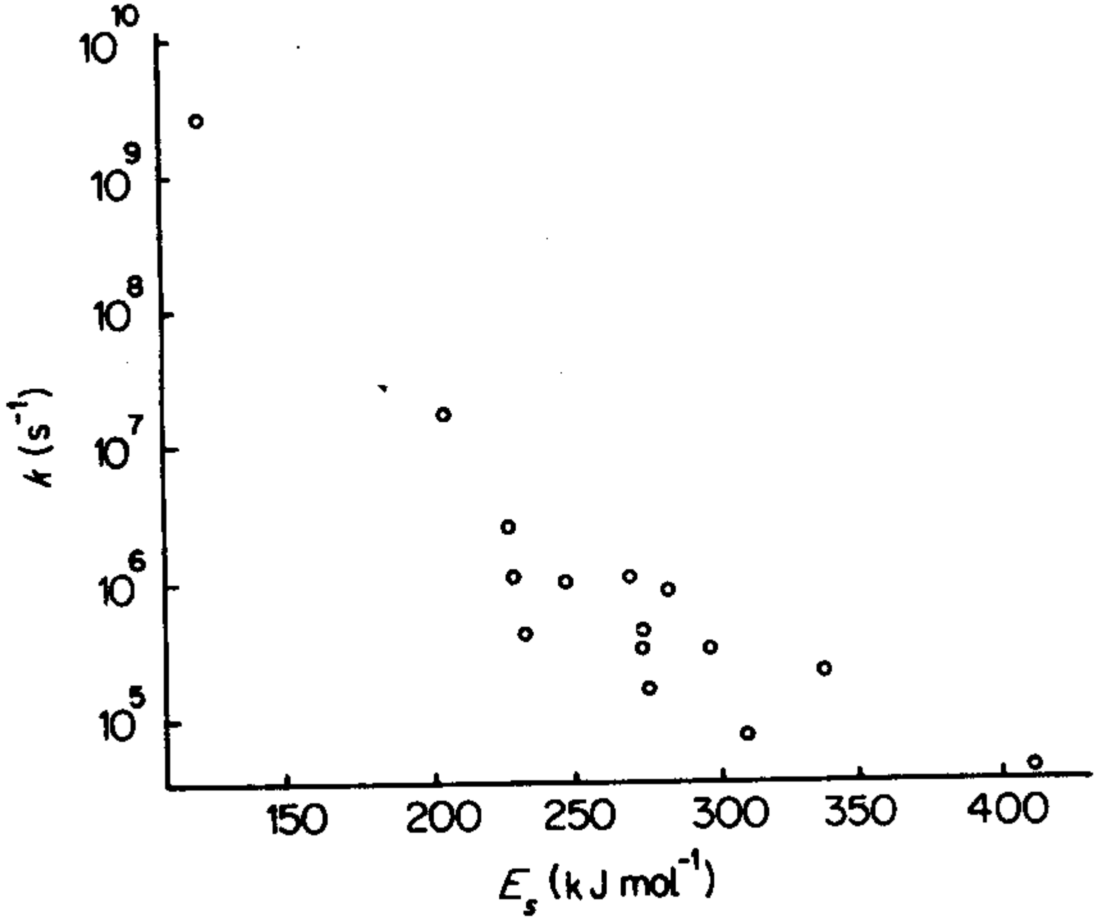
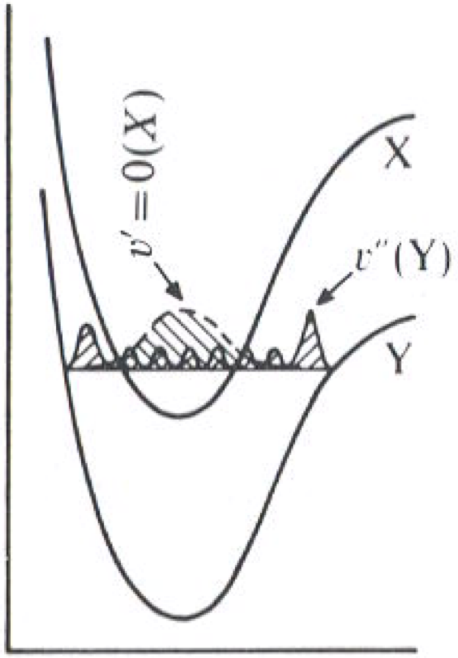
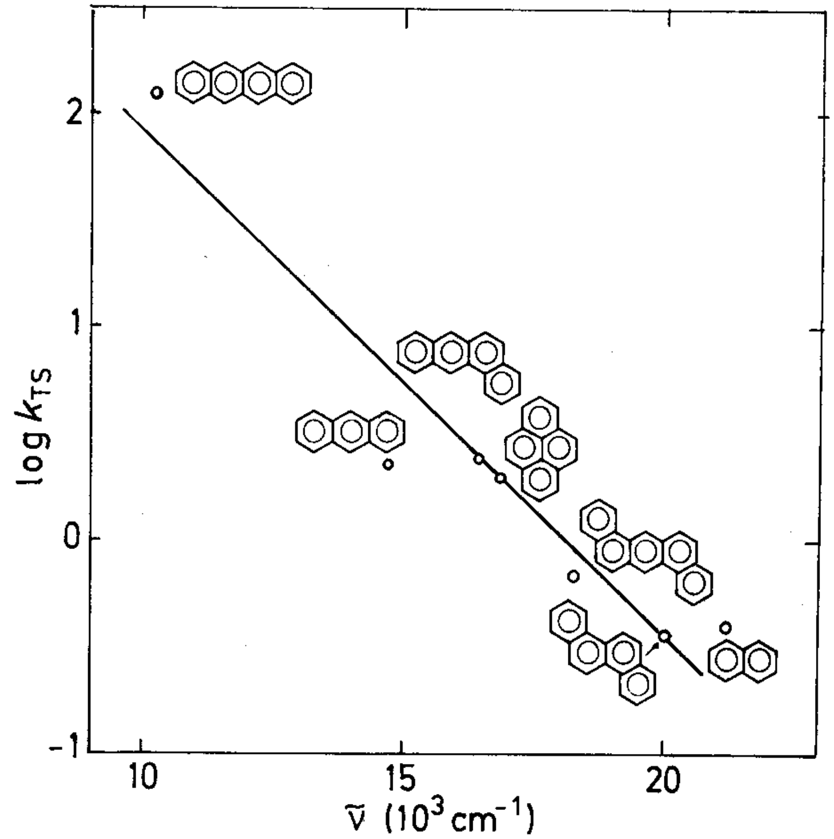


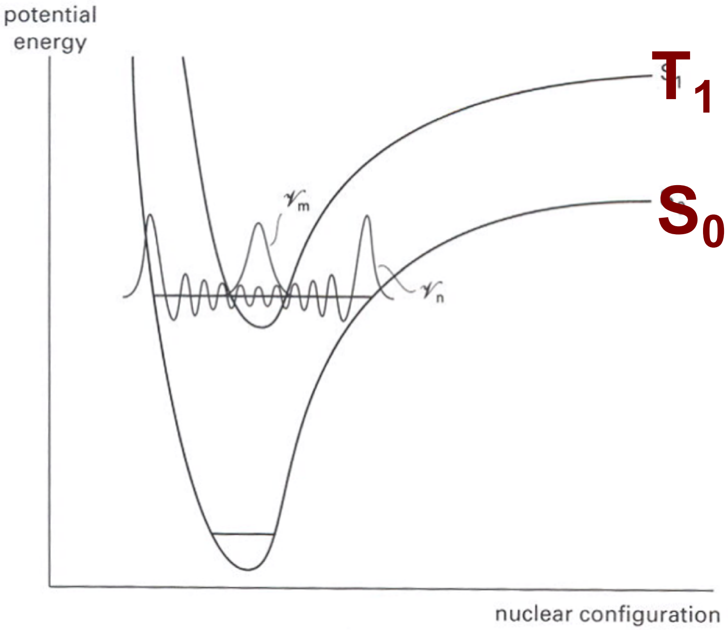
Figure 3.25. Singlet decay rate constants (k) of aromatic hydrocarbons plotted against the singlet energy (E_S). (From data in J. B. Birks, *Photophysics of Aromatic Molecules*, (1970), Wiley)



Dependence of rate of k_{ISC} T_1 to S_0 on energy gap



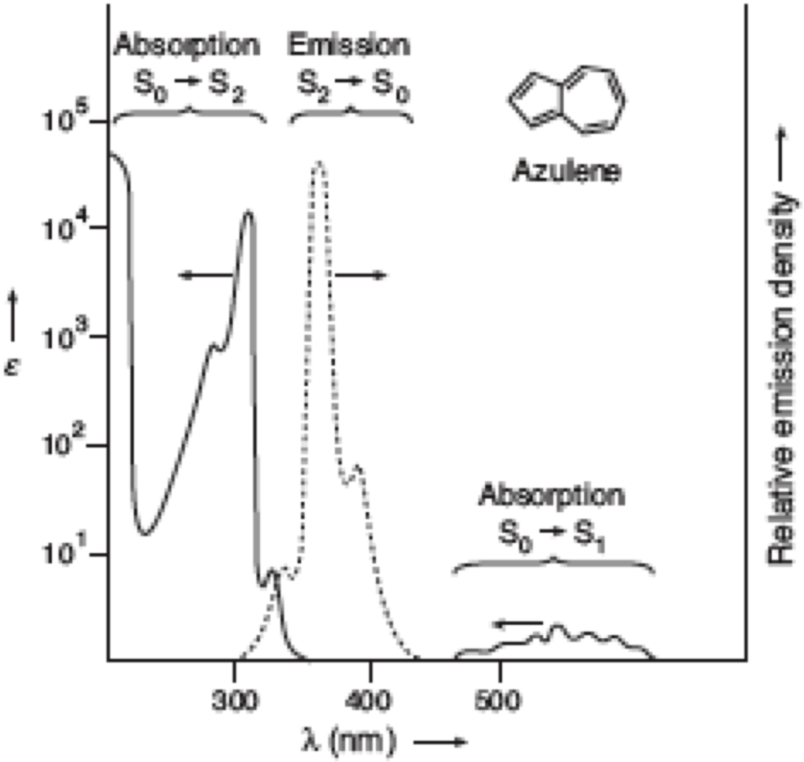
igure 5.5. Relationship between the energy gap $\Delta E(T_1 - S_0)$ and the logarithm of he rate constant k_{TS} of intersystem crossing in aromatic hydrocarbons (data from irks, 1970).

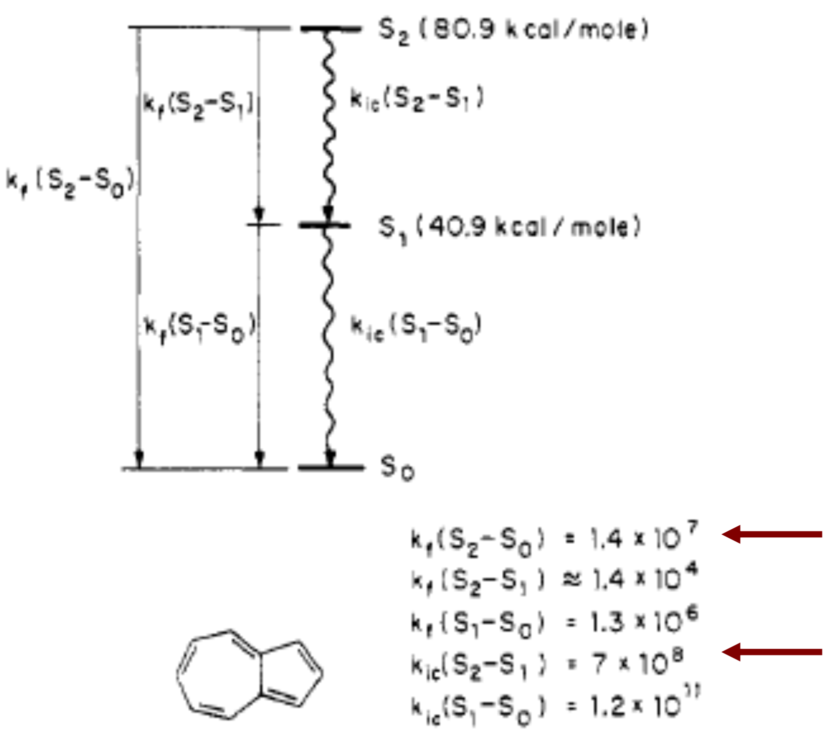


Overlap between lowest vib level of T_1 and high (degenerate) vib level of S_0)

Azulene Anamoly and Energy Gap Law

Fluorescence occurs only from S_1 to S_0; phosphorescence occurs only from T_1 to S_0; S_n and T_n emissions are extremely rare (Kasha's rule).





$k_f(S_2-S_0) = 1.4 \times 10^7$

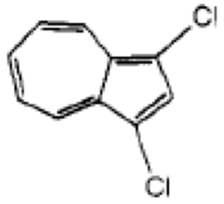
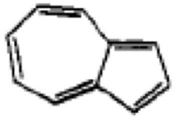
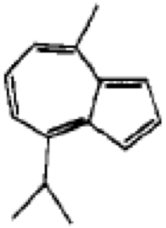
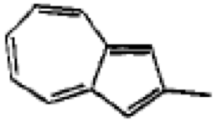
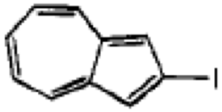
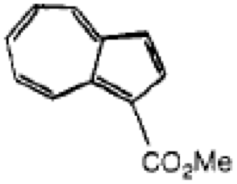
$k_f(S_2-S_1) \approx 1.4 \times 10^4$

$k_f(S_1-S_0) = 1.3 \times 10^6$

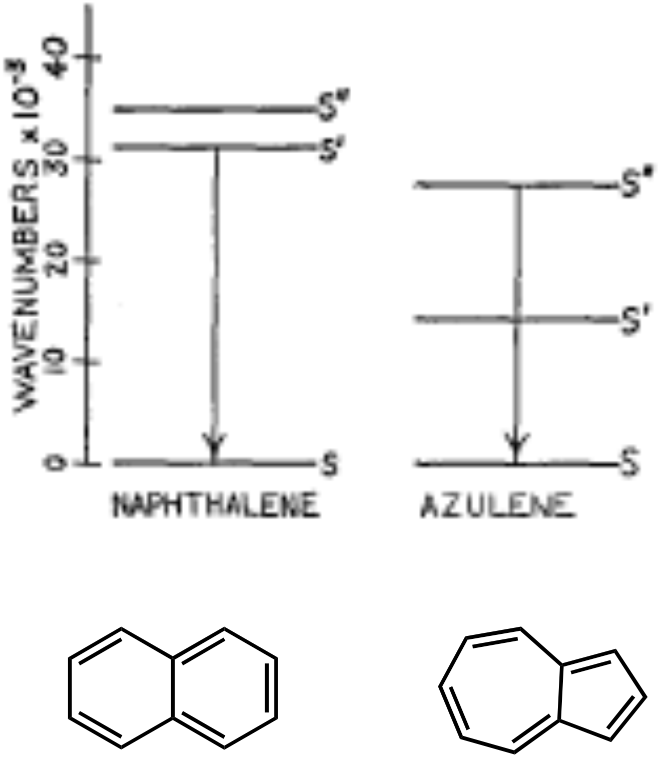
$k_{ic}(S_2-S_1) = 7 \times 10^8$

$k_{ic}(S_1-S_0) = 1.2 \times 10^{11}$

TABLE I. Fluorescence Quantum Yields and the Energies of the First Two Excited Singlet States of Substituted Azulenes[a]

	Φ_{fl}	E_{S_1}, kcal/mol	E_{S_2}, kcal/mol	ΔE, kcal/mol
	0.058	36.3	77.0	40.9
	0.031	40.9	80.9	40.0
	0.014	39.5	77.8	38.3
	0.0081	42.6	79.5	36.9
	0.0034	42.9	77.5	34.6
	$\sim 10^{-4}$	44.3	77.2	32.9

S$_2$ to S$_1$ rate vs Energy Gap



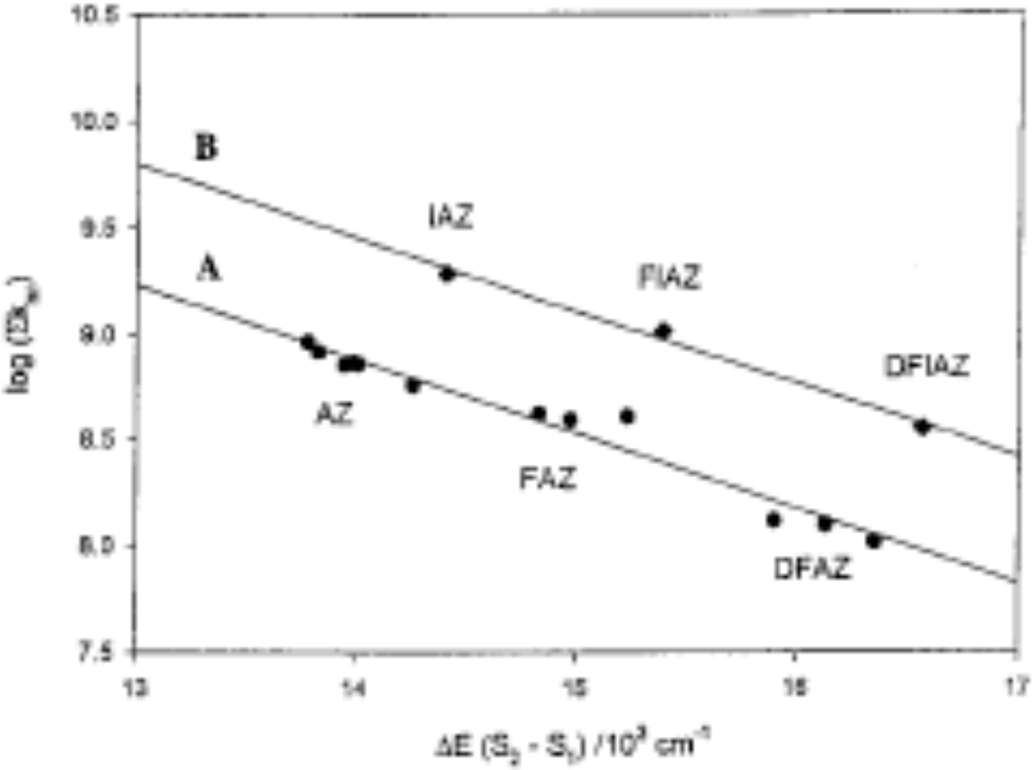


Figure 3. Log−linear energy gap law plots (see text) for azulene (AZ), 1-fluoroazulene (FAZ), and 1,3-difluoroazulene (DFAZ) in several solvents (line A), and for 6-isopropylazulene (IAZ), 1-fluoro-6-isopropylazulene (FIAZ), and 1,3-difluoro-6-isopropylazulene in *n*-hexane (line B). The data for AZ in several solvents are taken from ref 11.

Effect of deuteration on radiationless process (T_1 to S_0)

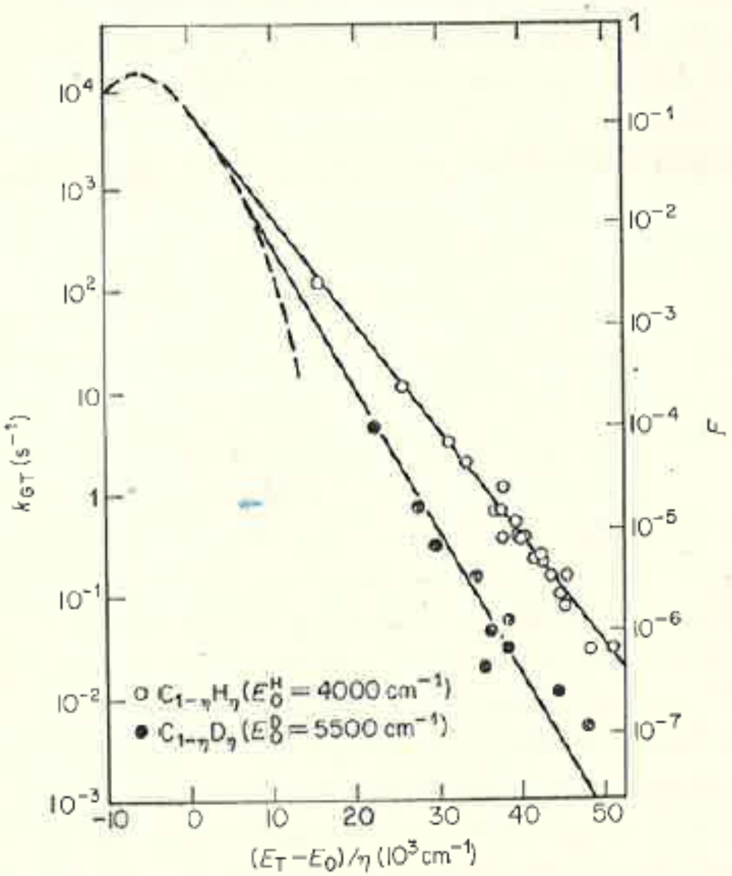


Figure 5.2 $T_1 - S_0$ intersystem crossing rate k_{GT} (s^{-1}) and Franck-Condon factor F against normalized triplet state energy $(E_T - E_0)/\eta$ for unsubstituted perprotonated and perdeuterated aromatic hydrocarbons. The broken line represents F as derived from phosphorescence spectra. The F-scale is normalized by drawing the two solid lines as tangents to this function (after Siebrand[8])

Birks book

Electronic to Vibrational Energy Transfer

Bond Type	Vibrational Type	Frequency
C=C	stretch	2200 cm^{-1}
C=O	stretch	1700 cm^{-1}
C=C	stretch	1600 cm^{-1}
N=N	stretch	1500 cm^{-1}
C-H	bend	1000 cm^{-1}
C-C	stretch	1000 cm^{-1}
C-C	bend	500 cm^{-1}
C-H	**stretch**	**3000 cm^{-1}**
C-D	**stretch**	**2100 cm^{-1}**

Isotope Effect on Rate of T_1 to S_0

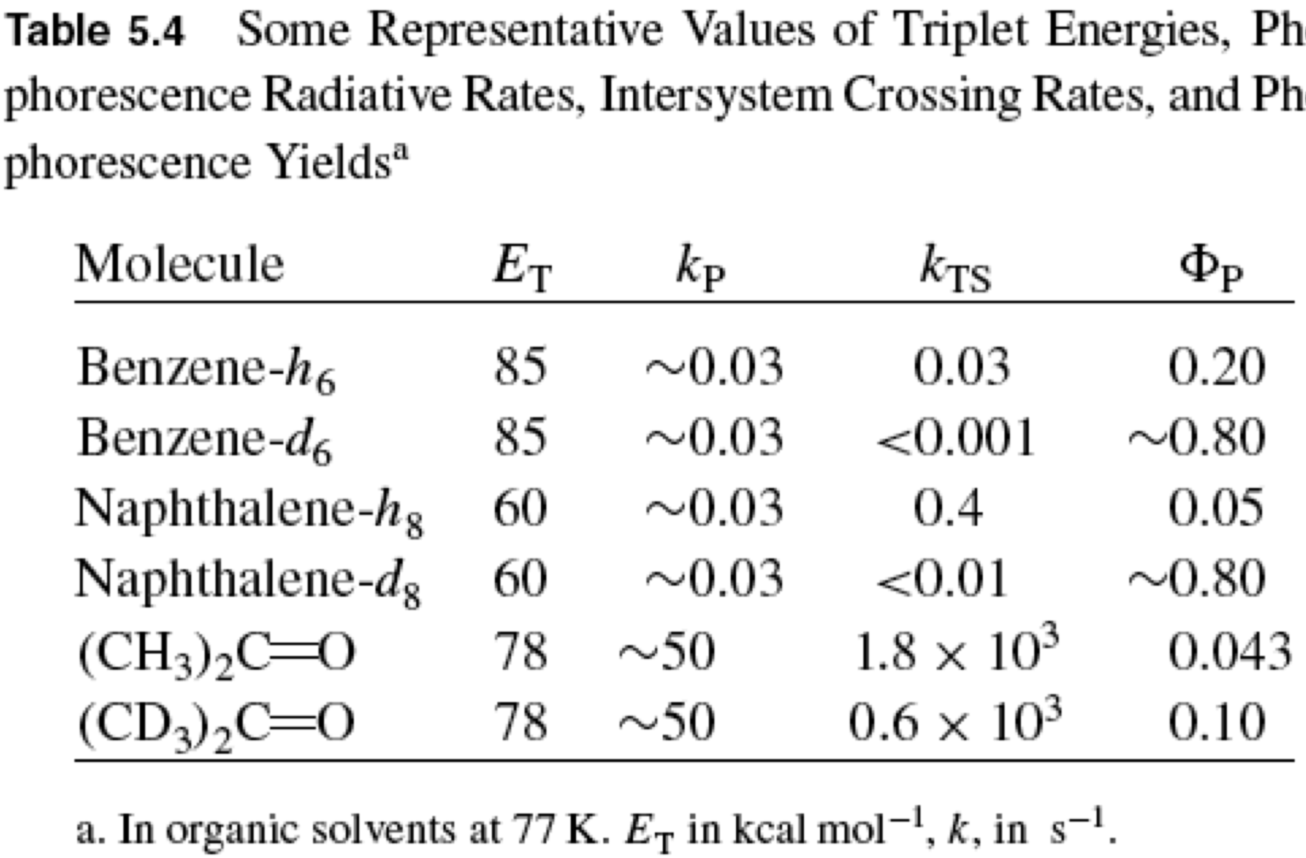
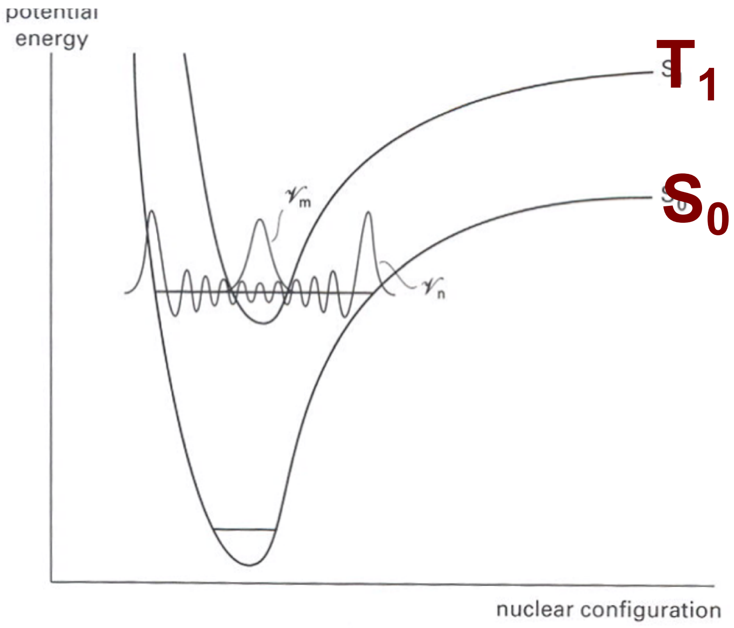


Table 5.4 Some Representative Values of Triplet Energies, Phosphorescence Radiative Rates, Intersystem Crossing Rates, and Phosphorescence Yields[a]

Molecule	E_T	k_P	k_{TS}	Φ_P
Benzene-h_6	85	~0.03	0.03	0.20
Benzene-d_6	85	~0.03	<0.001	~0.80
Naphthalene-h_8	60	~0.03	0.4	0.05
Naphthalene-d_8	60	~0.03	<0.01	~0.80
$(CH_3)_2C{=}O$	78	~50	1.8×10^3	0.043
$(CD_3)_2C{=}O$	78	~50	0.6×10^3	0.10

a. In organic solvents at 77 K. E_T in kcal mol^{-1}, k, in s^{-1}.

C-H stretch	**3000 cm^{-1}**
C-D stretch	**2100 cm^{-1}**



Vibrational effects on singlet oxygen lifetime

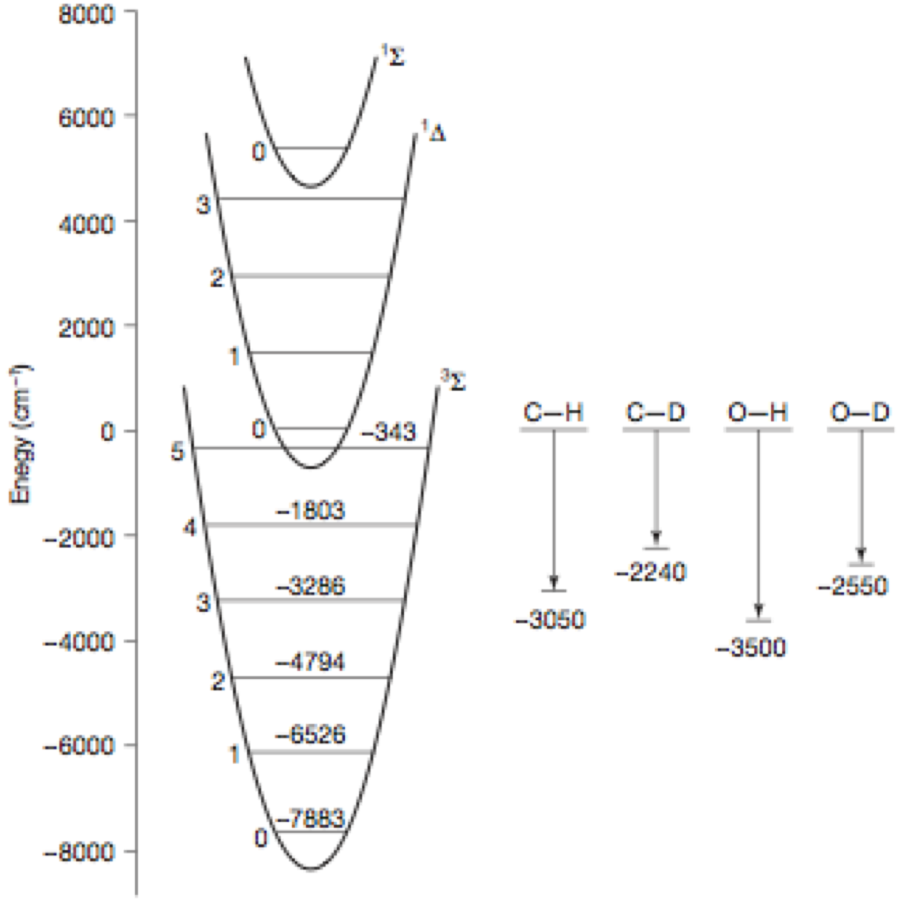


Figure 14.3 Comparison of the energy levels of $^1\Delta$ to common high frequency X—H and X—D vibrations of solvents. Energies in cm^{-1}.

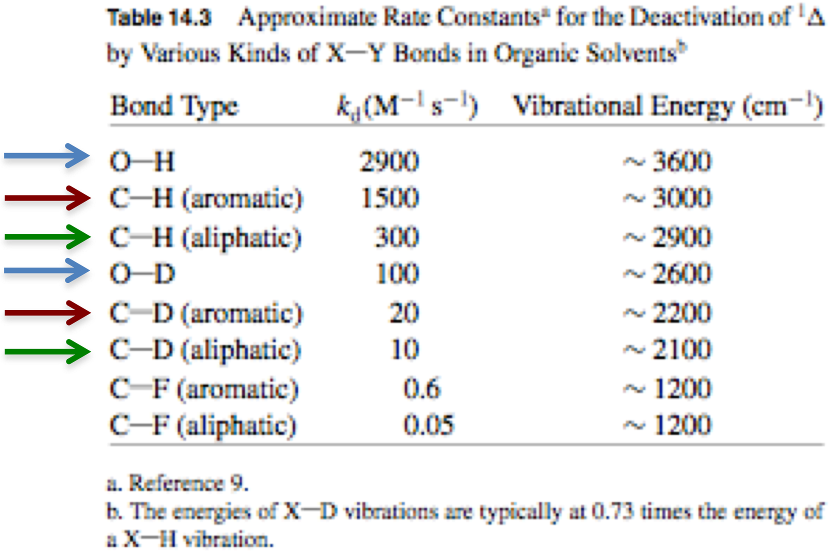
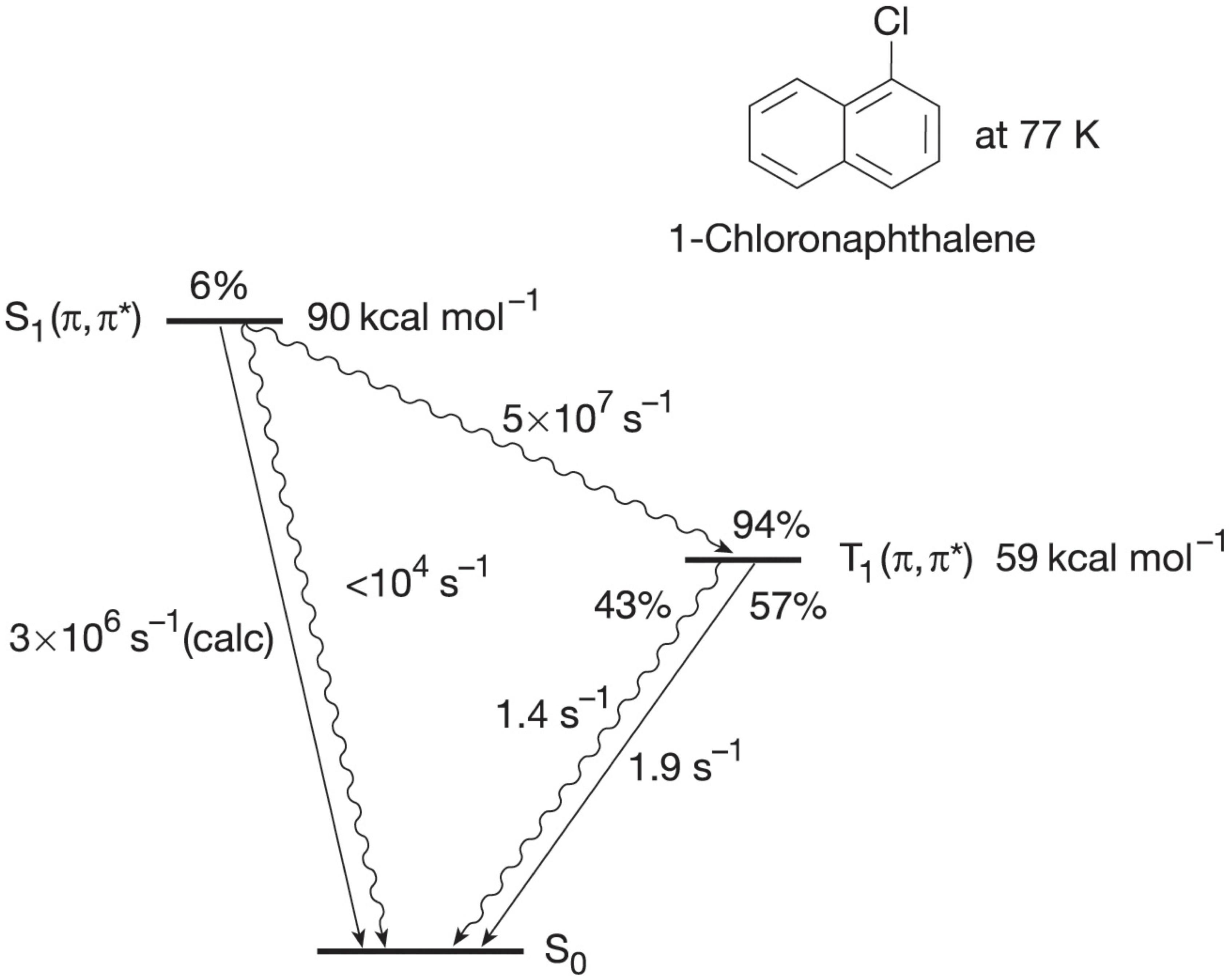


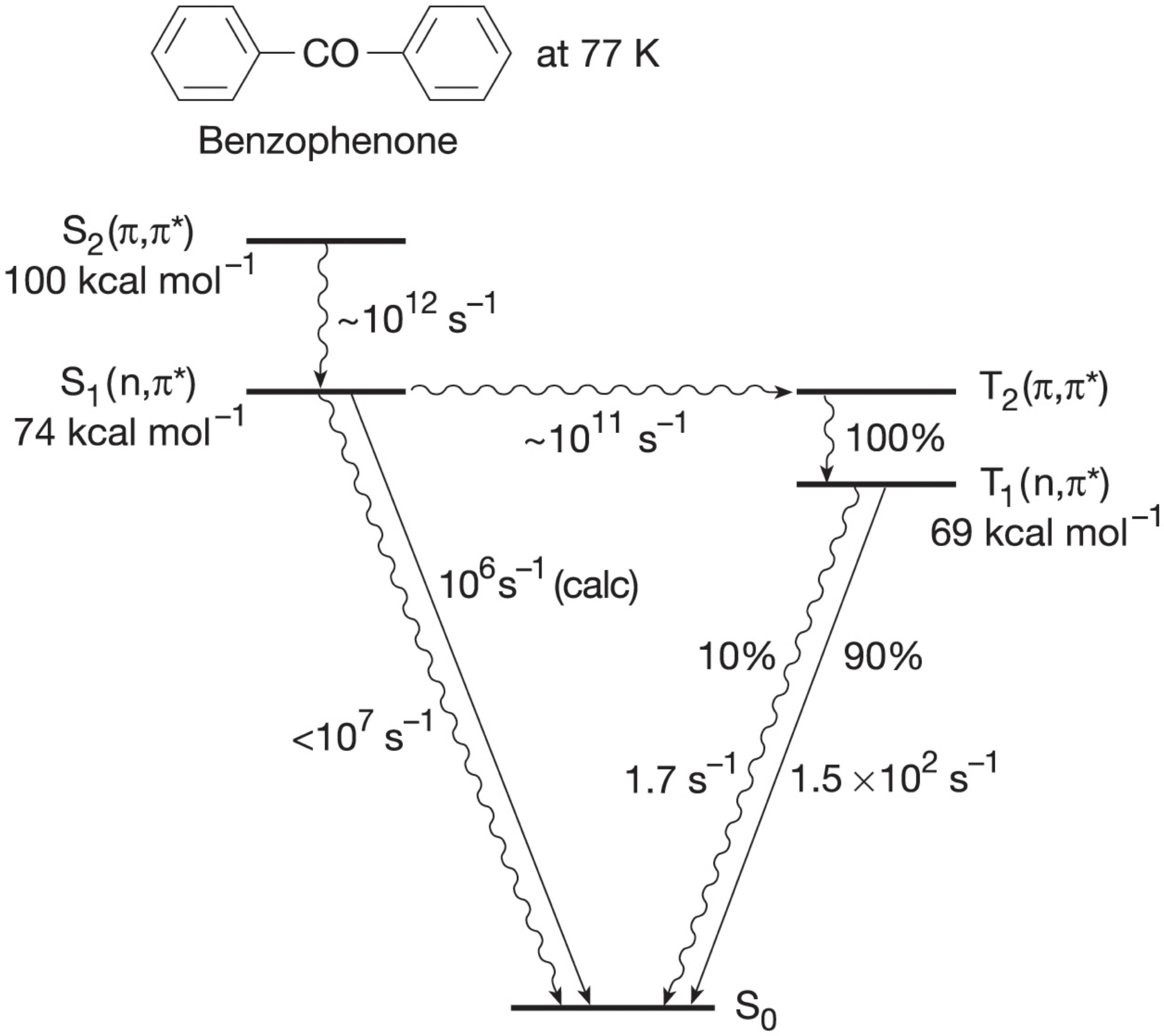
Table 14.3 Approximate Rate Constants[a] for the Deactivation of $^1\Delta$ by Various Kinds of X—Y Bonds in Organic Solvents[b]

Bond Type	k_d (M^{-1} s^{-1})	Vibrational Energy (cm^{-1})
O—H	2900	~ 3600
C—H (aromatic)	1500	~ 3000
C—H (aliphatic)	300	~ 2900
O—D	100	~ 2600
C—D (aromatic)	20	~ 2200
C—D (aliphatic)	10	~ 2100
C—F (aromatic)	0.6	~ 1200
C—F (aliphatic)	0.05	~ 1200

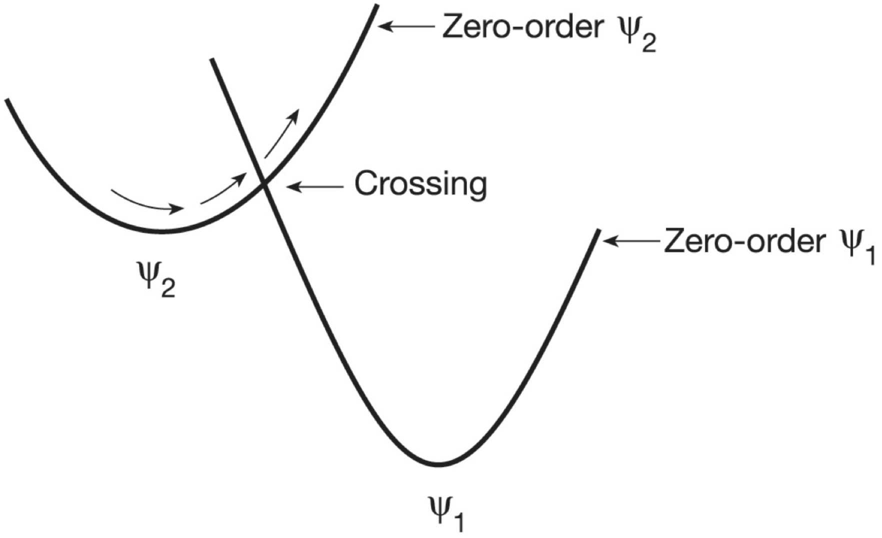
a. Reference 9.

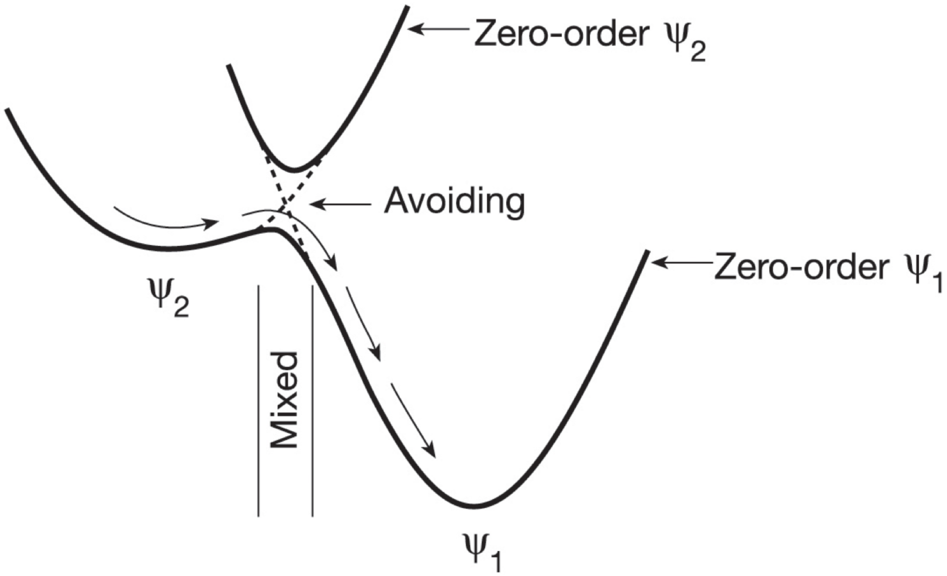
b. The energies of X—D vibrations are typically at 0.73 times the energy of a X—H vibration.

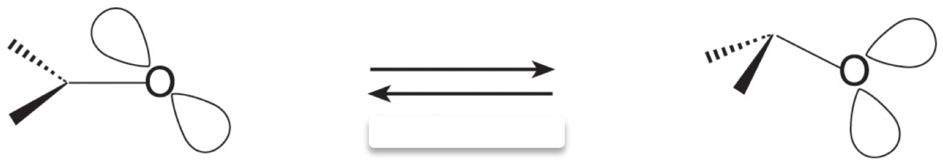

Cl
at 77 K
1-Chloronaphthalene
6%
S1 (π, π*)
90 kcal mol−1
5×10^7 s−1
94%
T1 (π, π*)
59 kcal mol−1
<10^4 s−1
3×10^6 s−1(calc)
43%
57%
1.4 s−1
1.9 s−1
S0


CO
at 77 K
Benzophenone
S2(π,π*)
100 kcal mol−1
~10¹² s−1
S1(n,π*)
74 kcal mol−1
~10¹¹ s−1
T2(π,π*)
100%
T1(n,π*)
69 kcal mol−1
10⁶s−1 (calc)
<10⁷ s−1
10%
90%
1.7 s−1
1.5 ×10² s−1
S0

Crossing from one to another surface depends on the allowedness of the transition: (a) electronic and (b) spin







Strictly planar

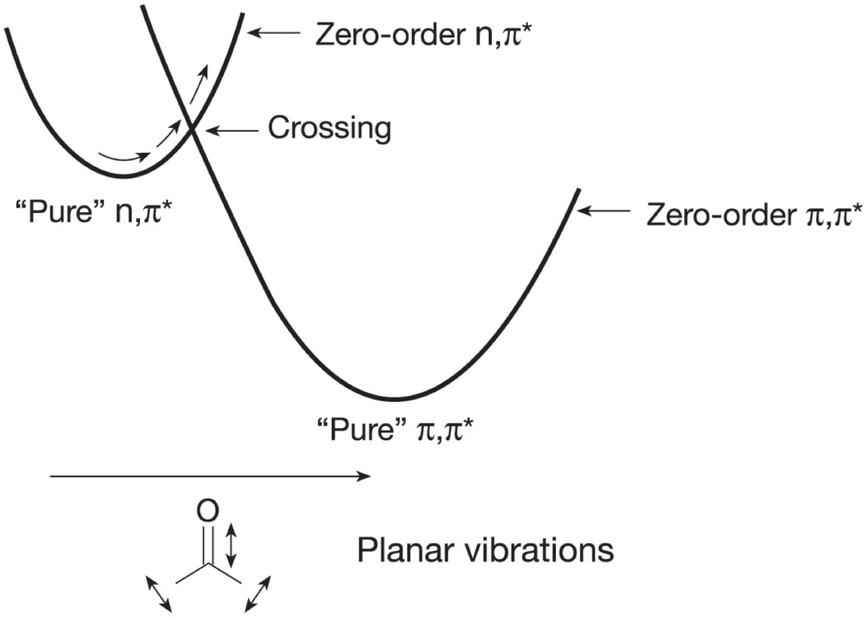
$n_0 = p_0$

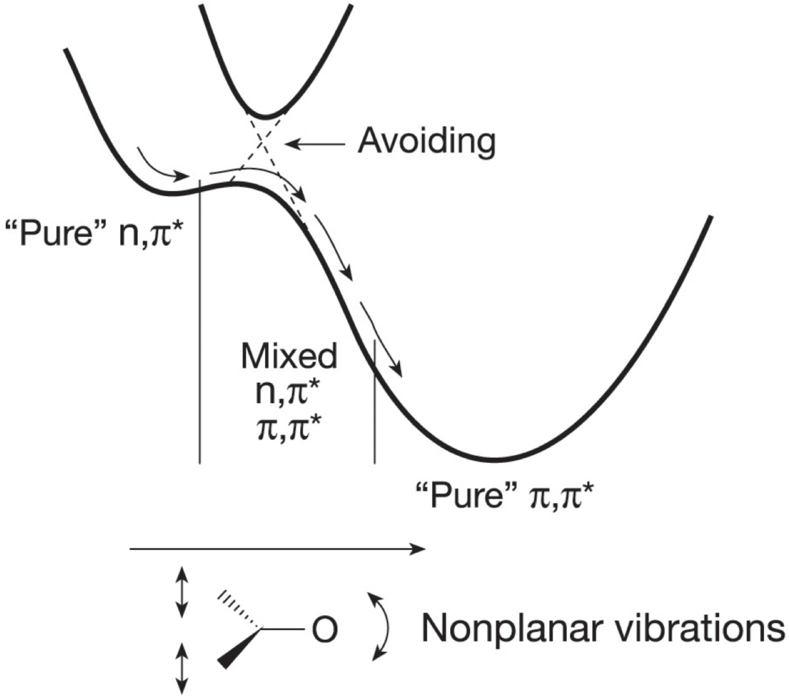
$\langle n_0 | \pi \rangle = 0$

Nonplanar

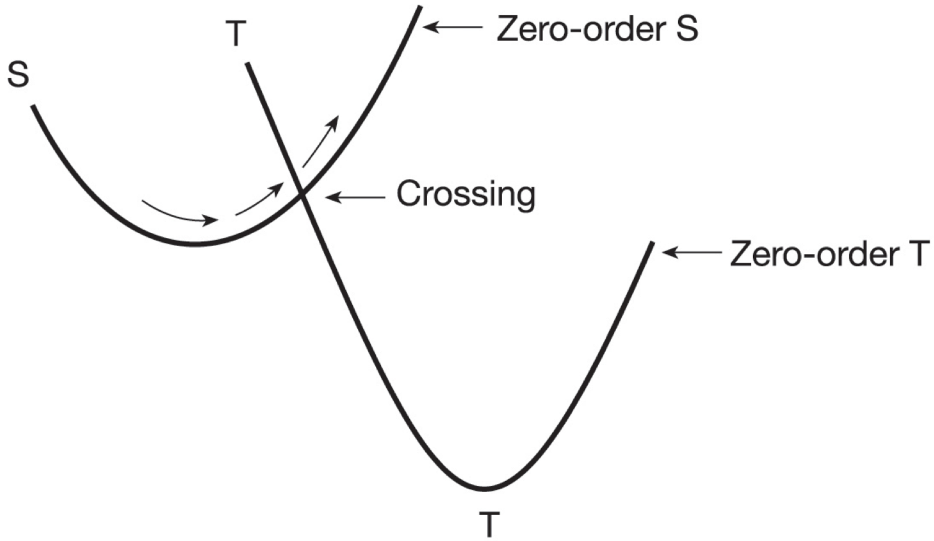
$n_0 = sp^n$

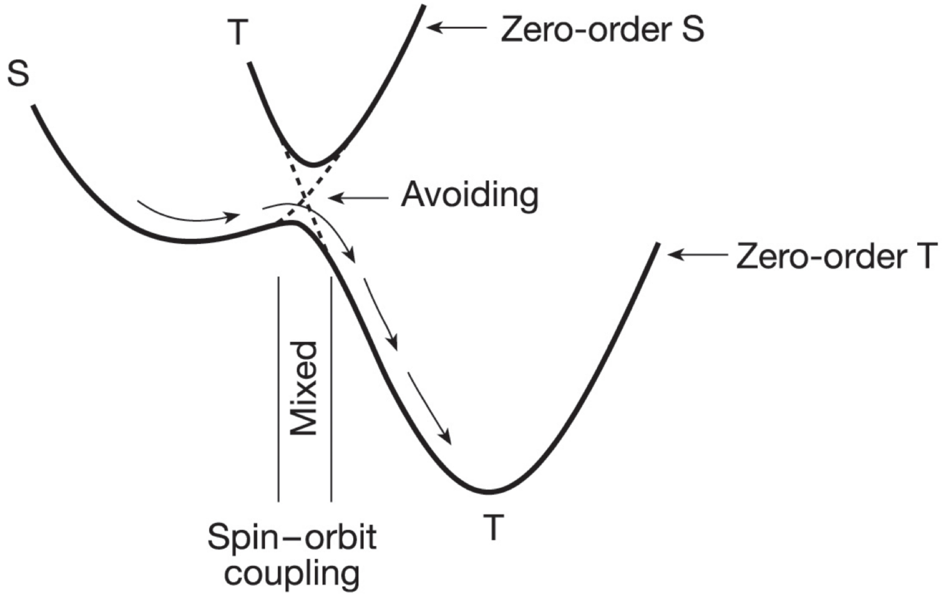
$\langle n_0 | \pi \rangle \neq 0$

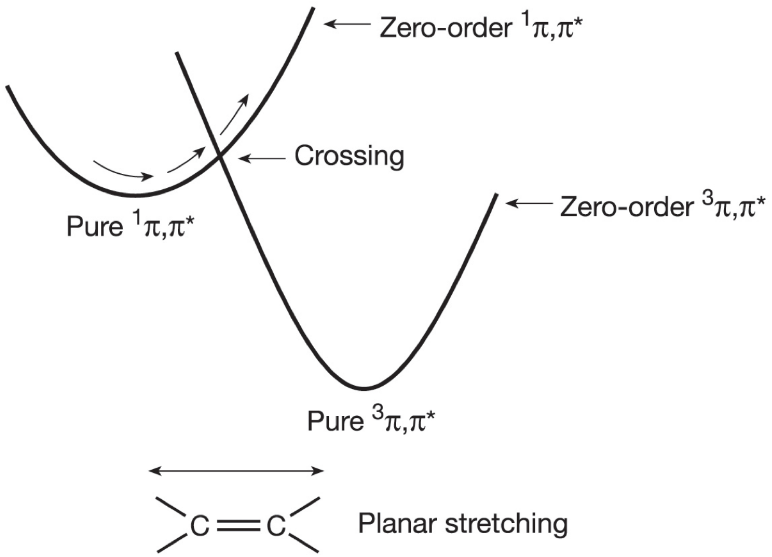


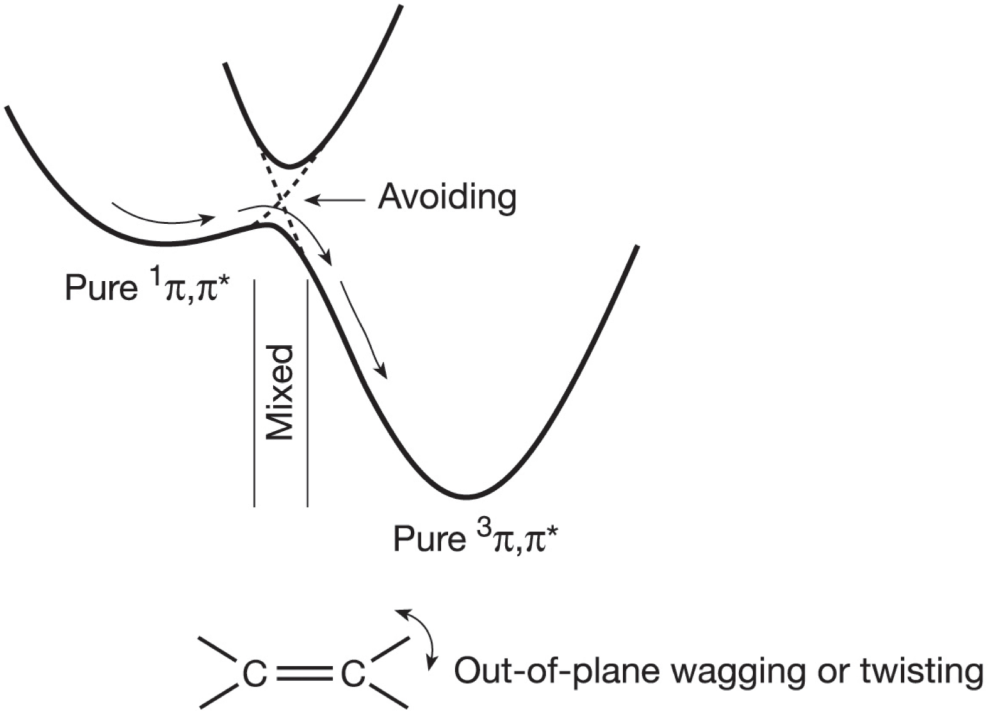


Role of Spin-Orbit Coupling on ISC

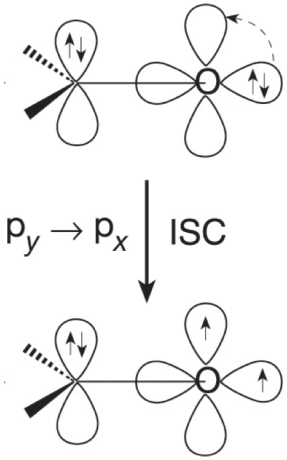





Zero-order $^1\pi,\pi^*$
Crossing
Zero-order $^3\pi,\pi^*$
Pure $^1\pi,\pi^*$
Pure $^3\pi,\pi^*$
C=C
Planar stretching


Avoiding
Pure $^1\pi,\pi^*$
Mixed
Pure $^3\pi,\pi^*$
C=C
Out-of-plane wagging or twisting

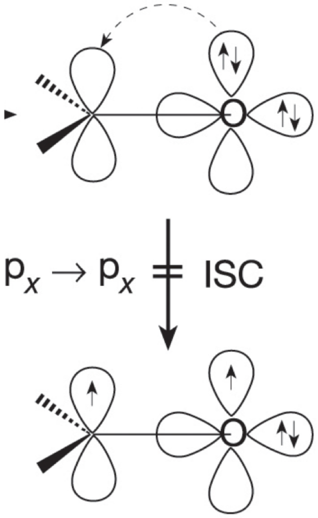
The Effect of Spin-Orbit Coupling on ISC



$$S_1 = \pi(\downarrow)\,n(\uparrow\downarrow)\,\pi^*(\uparrow) = {}^1(\pi,\pi^*)$$

Spin–flip allowed

$$T_1 = \pi(\uparrow\downarrow)\,n(\uparrow)\,\pi^*(\uparrow) = {}^3(n,\pi^*)$$

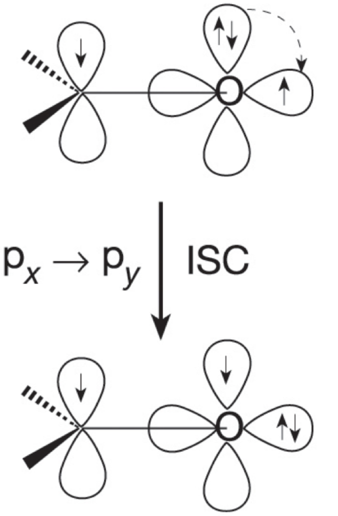


$$S_1 = \pi(\downarrow)\,n(\uparrow\downarrow)\,\pi^*(\uparrow) = {}^1(\pi,\pi^*)$$

Spin–flip forbidden

$$T_1 = \pi(\uparrow)\,n(\uparrow\downarrow)\,\pi^*(\uparrow) = {}^3(\pi,\pi^*)$$

The Effect of Spin-Orbit Coupling on ISC

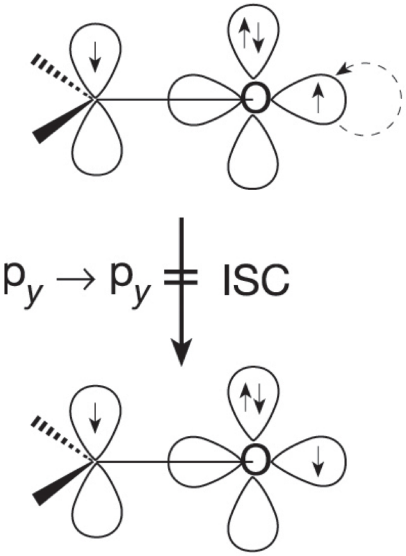


$S_1 = \pi(\uparrow\downarrow)n(\uparrow)\pi^*(\downarrow) = {}^1(n,\pi^*)$

Spin–flip allowed

ISC allowed

$T_1 = \pi(\downarrow)n(\uparrow\downarrow)\pi^*(\downarrow) = {}^3(\pi,\pi^*)$



$S_1 = n(\uparrow)\pi^*(\downarrow) = {}^1(n,\pi^*)$

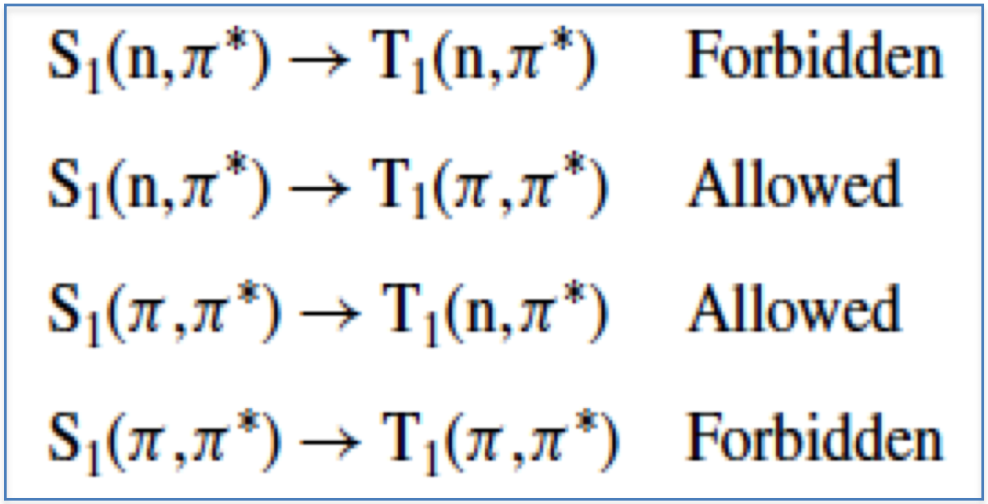
Spin–flip forbidden

ISC forbidden

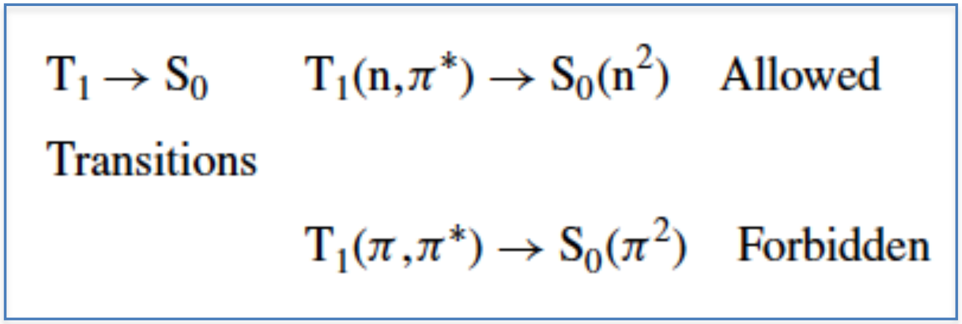
$T_1 = n(\downarrow)\pi^*(\downarrow) = {}^3(n,\pi^*)$

El-Sayed's Rule

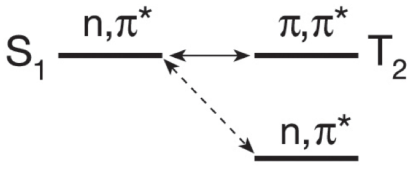
Intersystem crossing is likely to be very slow unless it involves a change of orbital configuration.



$S_1(n,\pi^*) \rightarrow T_1(n,\pi^*)$	Forbidden
$S_1(n,\pi^*) \rightarrow T_1(\pi,\pi^*)$	Allowed
$S_1(\pi,\pi^*) \rightarrow T_1(n,\pi^*)$	Allowed
$S_1(\pi,\pi^*) \rightarrow T_1(\pi,\pi^*)$	Forbidden

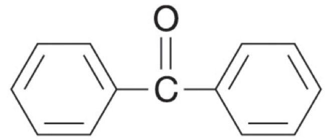


$T_1 \rightarrow S_0$ Transitions	$T_1(n,\pi^*) \rightarrow S_0(n^2)$	Allowed
	$T_1(\pi,\pi^*) \rightarrow S_0(\pi^2)$	Forbidden

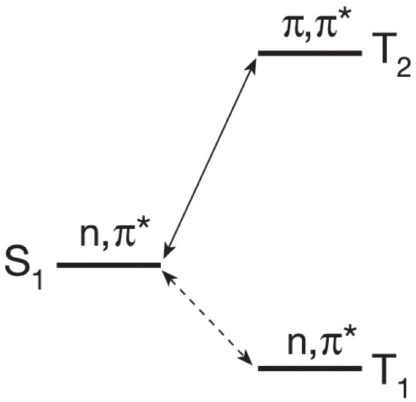


$k_{ST} \sim 10^{11}–10^{10}$ s^{-1}

“Fast”

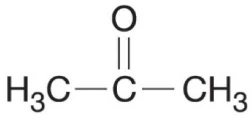


Benzophenone



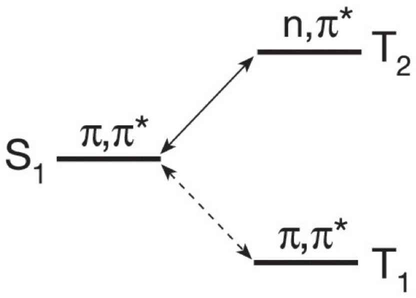
$k_{ST} \sim 10^{9}–10^{8}$ s^{-1}

“Intermediate”



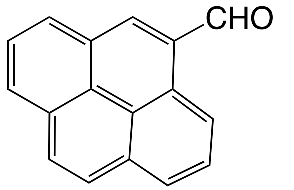
$H_3C-\overset{O}{\overset{\|}{C}}-CH_3$

Acetone



$k_{ST} \sim 10^{7}–10^{6}$ s^{-1}

“Slow”



Pyrenealdehyde

Spin-Orbit Coupling and Heavy Atom Effect

Field at a molecular level is generated from the *orbital motion* of the electron around the nucleus.

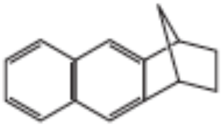
$$\hat{H}_{SO} = \zeta l \cdot s$$

$$\zeta_{n,l} \propto \frac{Z^4}{n^3 l(l + 1/2)(l + 1)}$$

The Spin-Orbit coupling constant depends on the fourth power of the atomic number and its effect is very large for heavy atoms.

Influence of Heavy Atom Effect on ISC

Molecule	k_F^0	k_{ST}	k_P^0	k_{TS}	Φ_F	Φ_P
Naphthalene	10^6	10^6	10^{-1}	10^{-1}	0.55	0.05
1-Fluoronaphthalene	10^6	10^6	10^{-1}	10^{-1}	0.84	0.06
1-Chloronaphthalene	10^6	10^8	10	10	0.06	0.54
1-Bromonaphthalene	10^6	10^9	50	50	0.002	0.55
1-Iodonaphthalene	10^6	10^{10}	500	100	0.000	0.70



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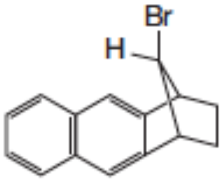
$k_{ST} = 2 \times 10^6\ \mathrm{s}^{-1}$

$k_{TS} = 2 \times 10^{-1}\ \mathrm{s}^{-1}$



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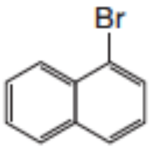
$k_{ST} = 300 \times 10^6\ \mathrm{s}^{-1}$

$k_{TS} = 40 \times 10^{-1}\ \mathrm{s}^{-1}$



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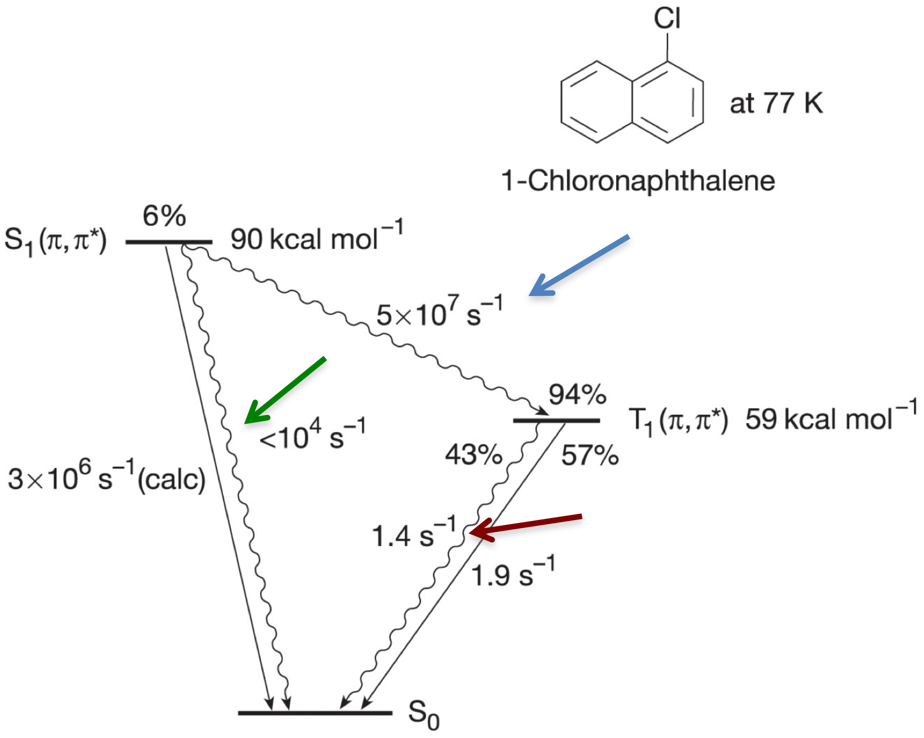
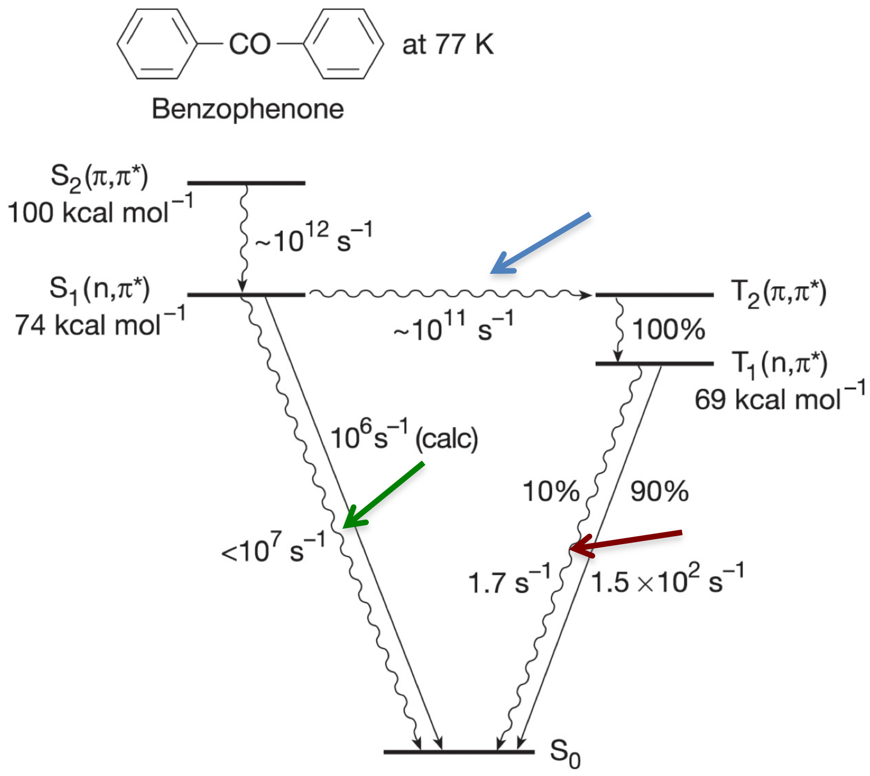
$k_{ST} = 500 \times 10^6\ \mathrm{s}^{-1}$

$k_{TS} = 600 \times 10^{-1}\ \mathrm{s}^{-1}$


Cl
at 77 K
1-Chloronaphthalene
S₁(π,π*)
6%
90 kcal mol⁻¹
5×10⁷ s⁻¹
<10⁴ s⁻¹
3×10⁶ s⁻¹(calc)
94%
T₁(π,π*) 59 kcal mol⁻¹
43%
57%
1.4 s⁻¹
1.9 s⁻¹
S₀


CO
at 77 K
Benzophenone
S₂(π,π*)
100 kcal mol⁻¹
~10¹² s⁻¹
S₁(n,π*)
74 kcal mol⁻¹
~10¹¹ s⁻¹
T₂(π,π*)
100%
T₁(n,π*)
69 kcal mol⁻¹
10⁶s⁻¹ (calc)
<10⁷ s⁻¹
10%
90%
1.7 s⁻¹
1.5×10² s⁻¹
S₀